NREL
Transforming ENERGY

MEA Manufacturing R&D

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National Renewable Energy Laboratory
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DOE Hydrogen and Fuel Cells Program
2019 Annual Merit Review and Peer Evaluation Meeting

Project ID: ta001

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

Overview

Timeline

Start: July 2007

End: Project continuation and direction determined annually by DOE

% complete: N/A

Barriers

Barriers	Target
E: Lack of Improved Methods of Final Inspection of MEAs	$20/kW (2020) at 500,000 stacks/yr
H: Low Levels of Quality Control	

Budget and Funded Partners

Fiscal Year	Total Funding*	LBNL	CSM
2018 (received)	$776,000	$150,000	$50,000
2019 (planned)	$0	$0	$0

* Total funding is the sum of NREL and all funded partners; includes work shown in S. Mauger (ta008)

Relevance

- FCTO Multi-year R&D Plan – Manufacturing R&D milestones
- 2016 HTAC Annual Report
  - Challenges remain, including "Improvements in manufacturing processes and yield rates..."
- *Review of the Research Program of the U.S. DRIVE Partnership*, Fifth Report, The National Academies Press, Washington DC, 2017
  - The focus should be on materials, performance, durability, and, ultimately, on manufacturability.
  - U.S. DRIVE should encourage projects that address the use of real-time, in situ electro-analytical quality-control methods.
- Proton OnSite
  - "Not just about materials/performance: Manufacturing is its own science… need to achieve cost and uniformity at scale."
- Canada-Germany Workshop on Fuel Cell Component Quality, Freiburg, 2018 (attended by NREL's Dr. Peter Rupnowski)
  - "In-line detection at high yields," "Limited in-line QC methods"
  - "R&D to determine defect specification – what non-uniformity is a critical defect," "Lack of transfer functions (how given defect affects device performance)"
  - "Standardized methods"
  - ***Peter brought back four pages of notes on what QC was needed for!***

Approach

- Understand quality control needs from industry partners and forums
  - *Engage LTE/H_2@Scale community*
- Develop diagnostics
  - *Study underlying physics of excitation and material response*
  - *Use multi-physics modeling to guide development*
  - *Use a unique suite of in-situ testing capabilities to understand defect thresholds*
- Validate diagnostics in-line
- Transfer technology

***Annual Milestone Criteria:**

- Physical resolution of 100 µm or smaller
- Thickness range: 12-175 µm
- Speed at least 2 ft/min

Date	Milestone/Deliverable (status as of 3/4/19)	Complete
6/18	Determine the feasibility of using reflectance imaging to measure Pt loading (Go/No-go)	100%
9/18	Set up experimental test bed to study membrane thickness imaging	100%
3/19	Perform studies of electrode coating irregularities	75%
3/19	Perform initial inspection studies with LTE materials	90%
6/19	Perform multi-spectral thickness imaging of PEMFC and LTE membranes*	40%
9/19	Perform in situ and ex situ studies to understand the impact of pinholes	10%

Collaborations

Industry Collaborators

Objective: ensure we continue to get detailed input on manufacturing QC needs, prioritization of diagnostic development, feedback on technique capabilities, and pursue tech transfer

- **Gore (TSA):** in-line characterization of membrane production rolls and development of automated detection algorithms
- **GM (CRADA):** development of in-line inspection techniques
- **Mainstream Engineering (CRADA):** development of in-line inspection techniques, and in situ membrane defect studies
- **Proton OnSite:** QC development for LTE MEA materials and structures
- **Ludlow/PBI Performance Products:** in-line QC scanning

Labs and Academia

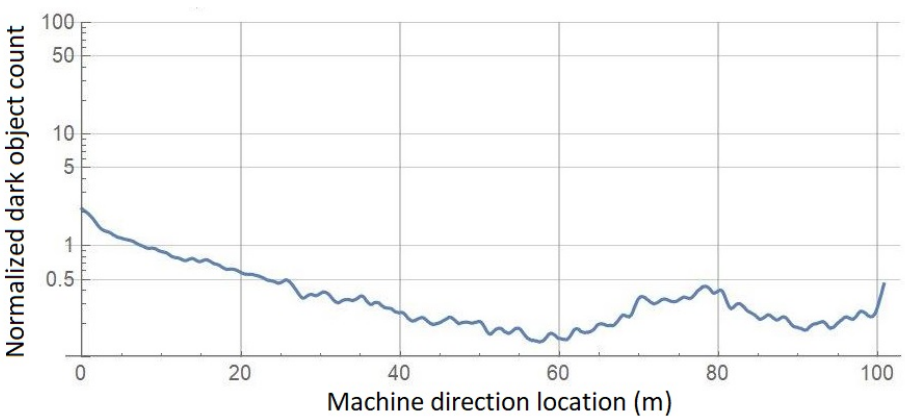
- **Lawrence Berkeley National Lab/Tufts University/UCI:** model development and integration, x-ray computed tomography
- **Colorado School of Mines:** diagnostics R&D, MEA ex situ characterization
- **National Research Council-Canada (NRC):** membrane inspection and coating

Accomplishments

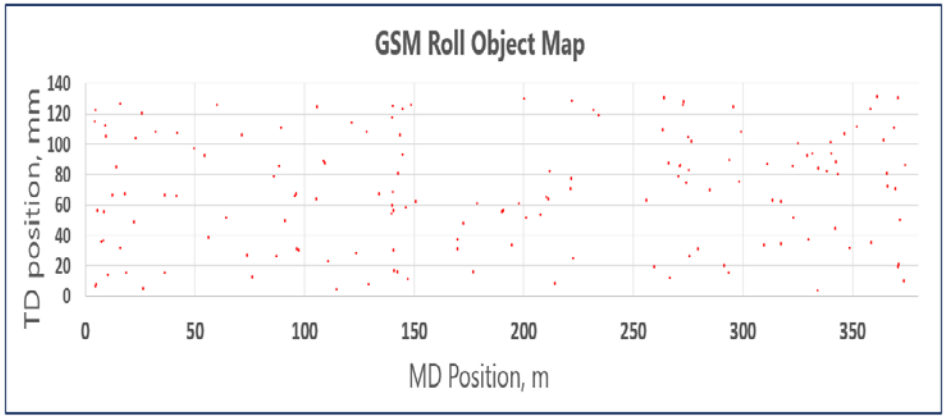
Completed in-line optical scanning of 1.6 km of GSM

Gore collaboration update: Gore-Select Membrane roll quality characterization

- Cost-shared project between Gore and FCTO
- Scanned a total of 14 rolls of GSM
  - Full width, full length, high-resolution (~15 µm x-y) scanning
  - Scanned a total length of 1.6 km!
- Provided machine- and transverse-direction metrics from automated algorithms
- Algorithm development: parallel-processing capabilities demonstrated on multi-core desktop and NREL HPC platforms
- Capability development: ability to modify depth of field to capture structured/non-flat membranes, improved RH control inside web-line hood



Full-length object count (based on specified detection threshold values)



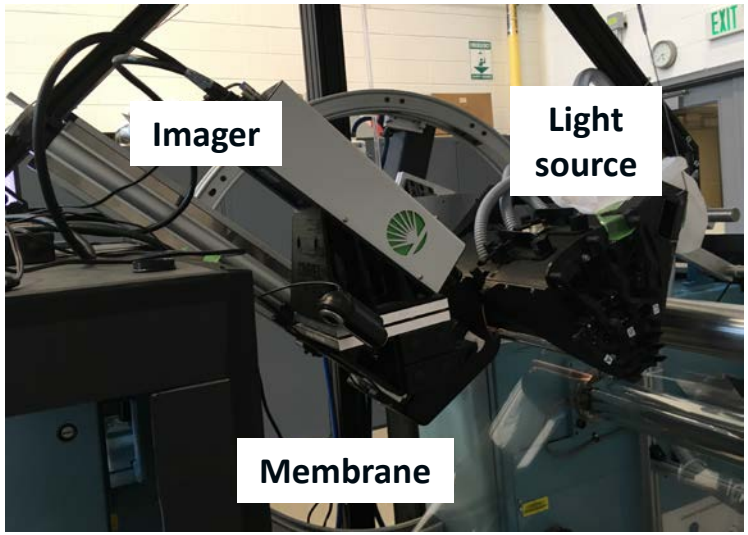
Full-web defect map (based on specified detection threshold values)

Accomplishments

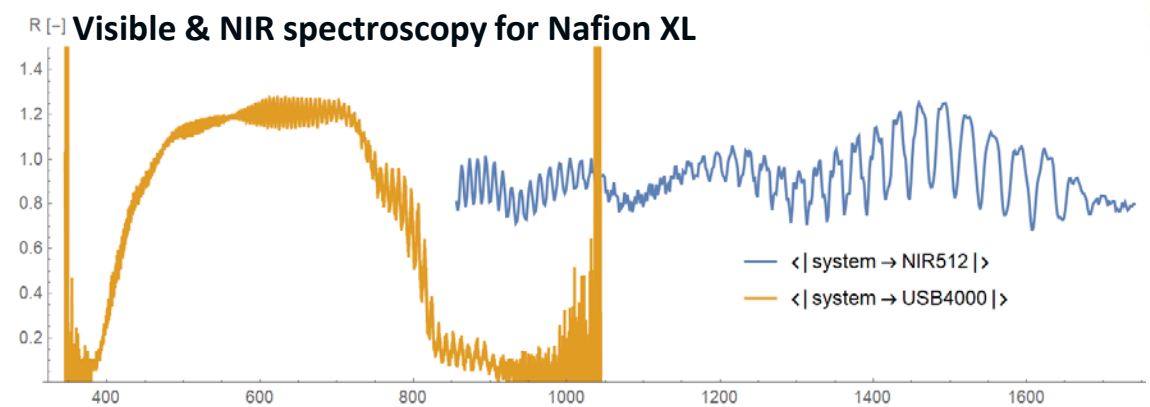
Continued development of thickness imaging technique

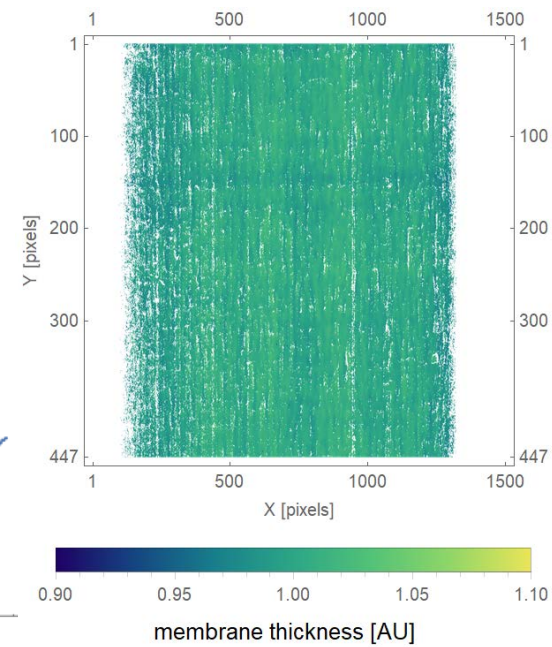
Update on multi-spectral imaging for in-line membrane thickness mapping

- Demonstrated the technique in-line at 5 fpm line speed
- Ran roll goods of Gore membrane
  - Resolution: x: 0.1 mm, y: 0.3 mm
- Also performed visible and NIR spectroscopy
  - Scoping studies on a wide set of membranes including: Nafion (XL, HP, 211, 212, 115, 117), 3M, CNRC, PBI, hydrocarbon, NREL-cast PFAEM
  - Thickness from <20 µm to >150 µm
  - Thicker (e.g. LTE) membranes require higher wavelength detector



Thickness imaging setup on web-line





Thickness map of section of Gore membrane

Accomplishments

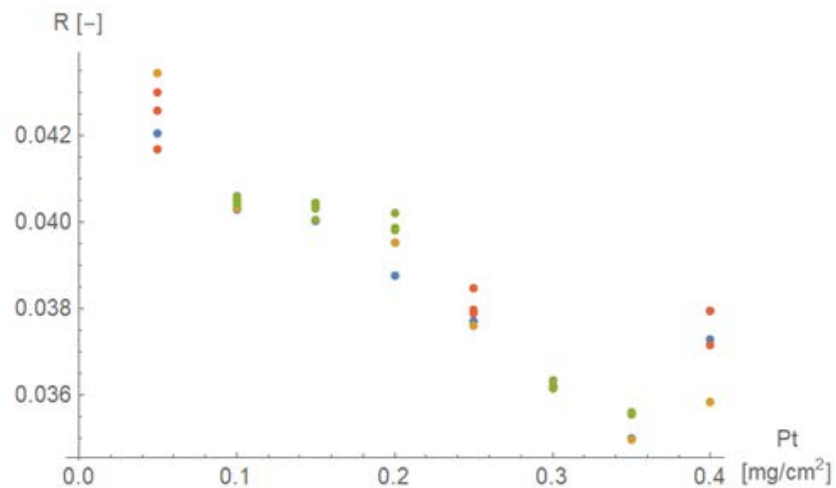
Demonstrated correlation between optical reflectance and loading

Optical imaging for electrode loading measurement

- Goal: *determine the feasibility of using an optical-reflectance based technique for imaging the loading of Pt in standard Pt/C electrodes*
- Study included 35 GDE and CCM samples, fabricated by two different processes
- Used two different optical imaging systems
- Demonstrated the target sensitivity of the technique for both CCMs and GDEs over most of the loading range
  - *Met the Go/No-go milestone*

Go/No-go Criteria:

- Loading range: 0.05-0.4 mg Pt/cm^2
- Sensitivity of ± 0.1 mg Pt/cm^2
- Speed at least 1 in/sec



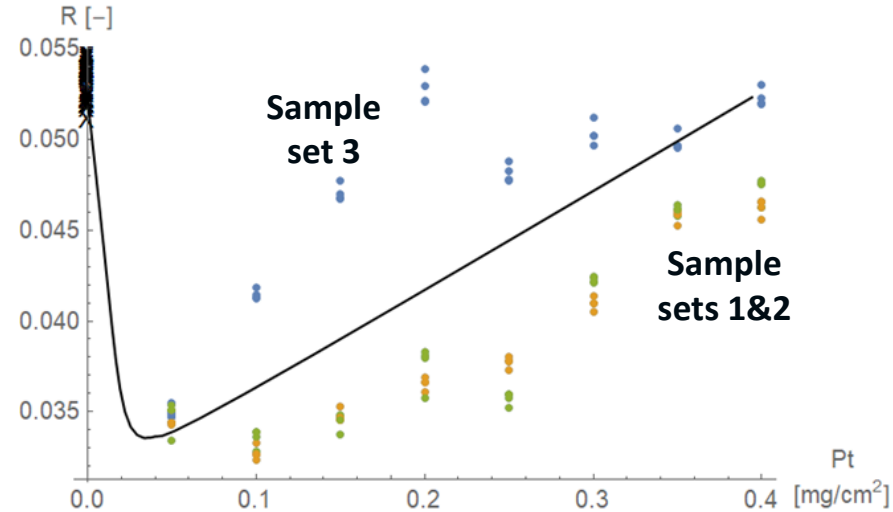
Reflectance response as a function of Pt loading for CCMs

Accomplishments

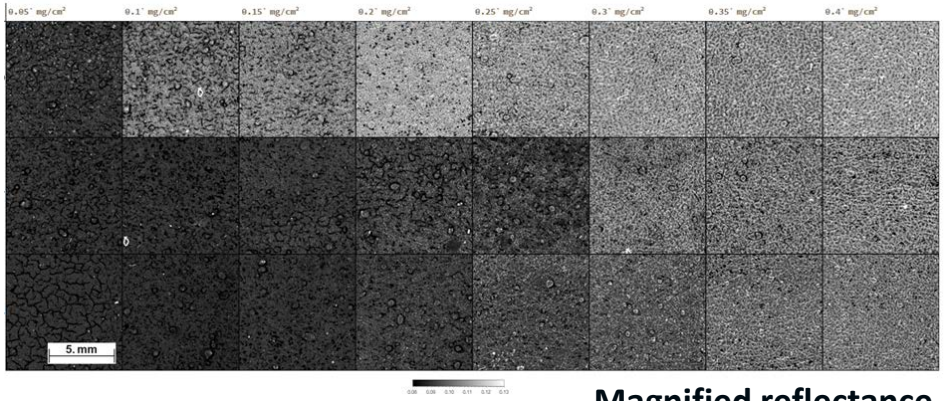
Optical measurements sensitive to loading, processing, morphology

Optical imaging for electrode loading measurement

- For GDEs, there were three sample sets: two made with one process, and one made with a second
  - Reflectance imaging was not only sensitive to loading, but to the differences in the process
- Transmittance mode also explored
  - Was very sensitive to loading in CCMs
  - Showed interesting aspects of electrode morphology

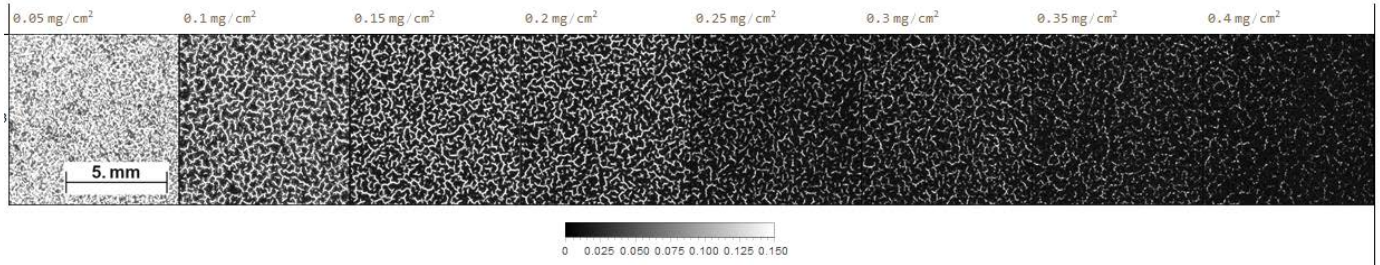


Reflectance response as a function of Pt loading for GDEs



Magnified reflectance images for three GDE sample sets: top – process 1, middle and bottom – process 2

Magnified transmittance images for CCMs indicating differences in macro morphology as a function of loading

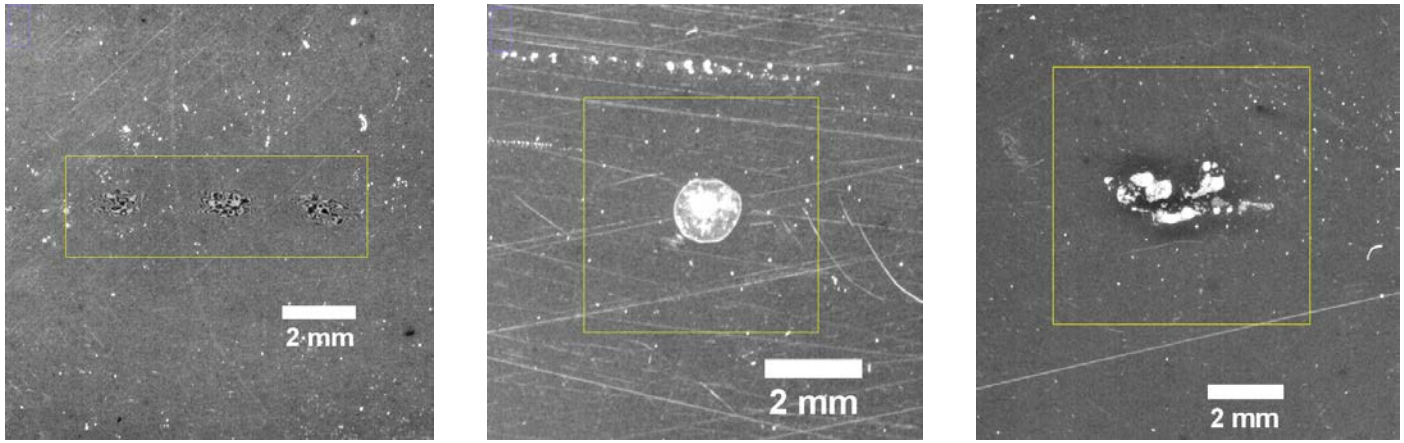


Accomplishments

Demonstrated that optical scanning tests are relevant to PBI film

Optical scanning of PBI membrane

- New industry collaboration with Ludlow Electrochemical Hardware and PBI Performance Products Inc.
- Goal is to leverage development of in-line high-resolution optical scanning and automated defect detection algorithms for in-line QC of PBI membrane roll goods
- Performed initial rapid optical scanning using small-sample test-bed on first set of samples
- Various surface features were able to be identified



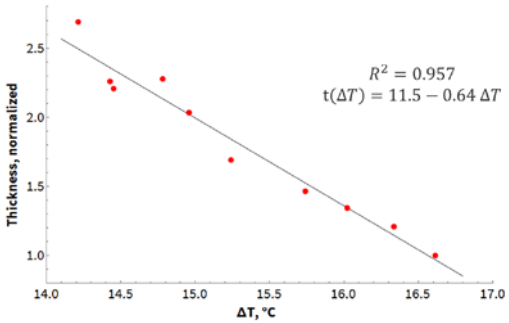
Example initial optical scanning results for the PBI Performance Products membrane

Accomplishments

Continued development of thermal scanning for half-cell membrane thickness

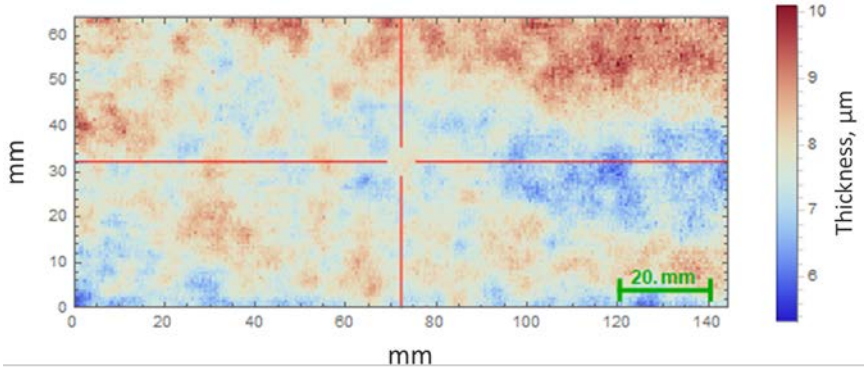
Update on thermal scanning for measurement of membrane thickness in half-cells (GM CRADA)

- Developed new methodology for mapping
  - Location-specific data from each IR imaging frame is processed
  - Processed data from each frame is stitched into temperature map
  - Temperature map transformed to thickness using empirical calibration from GM samples
- Future work
  - Understand impact of data-averaging parameters on resolution, and optimize
  - Validate technique with samples having varying thickness within the sample



Temperature-thickness calibration curve determined from series of 10 GM half cells with different membrane thickness (shown last year)

Cartoon of frame-by-frame data processing and stitching into temperature map



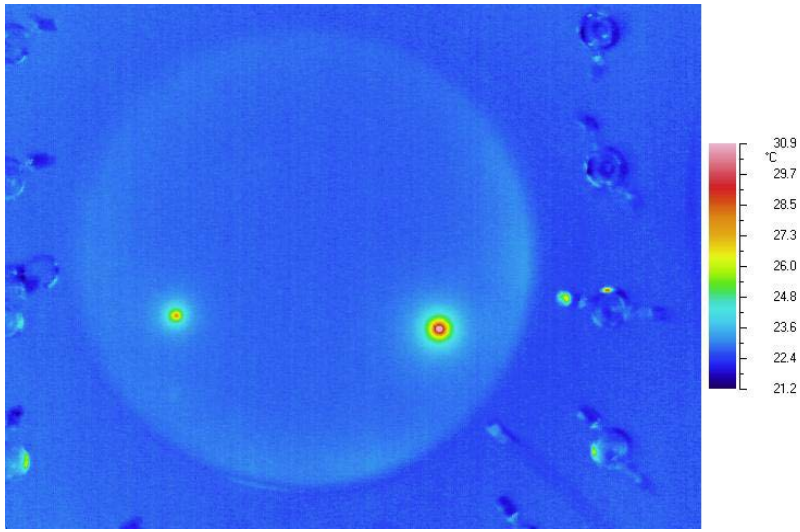
Thickness map of half cell with nominally 7 µm thick membrane

Accomplishments

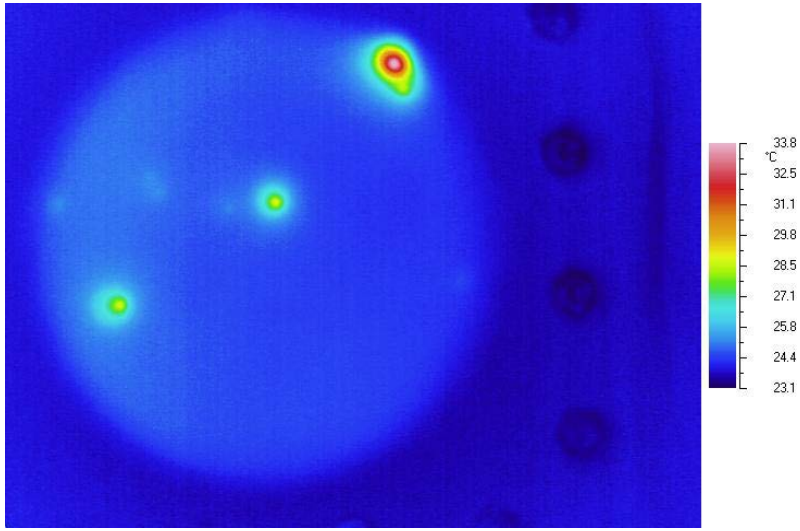
Demonstrated applicability of through-plane IR to LTE CCMs

Through-plane IR diagnostics for LTE CCMs

- Received CCMs from Proton
  - CCMs had been removed from operated stacks
  - Proton tested all CCMs with proprietary discharging test to identify suspected through-plane defects
- Performed two through-plane IR diagnostics
  - Direct-current excitation: shorts
    - No shorts detected
  - Reactive excitation: pinholes
    - Modified test-bed for LTE CCMs
    - Several CCMs tested positive
    - No false positives
    - NREL results confirmed the Proton results
- Benefit: identified the location/count of discrete defects



Thermal response using reactive excitation of two of the CCMs tested positive by Proton

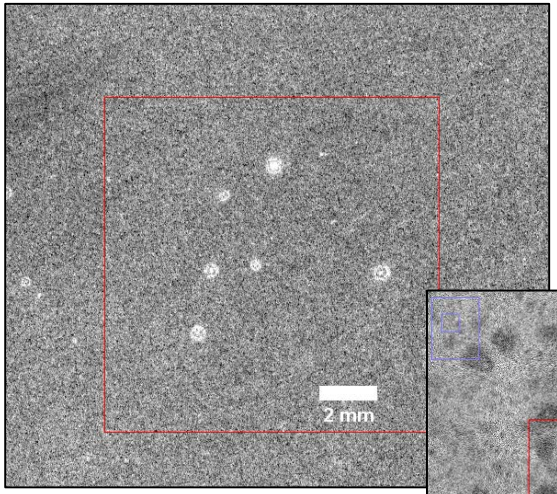


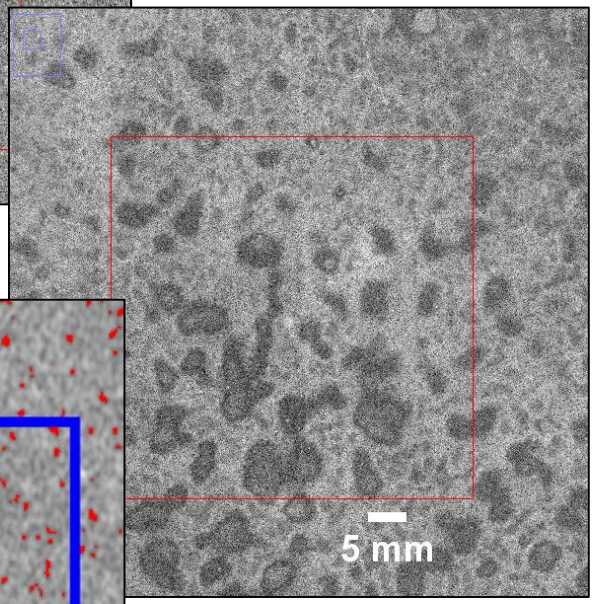
Accomplishments

Demonstrated applicability of optical scanning to LTE PTLs

Optical scanning of LTE PTLs

- Pristine and defected coated Ti PTLs provided by Proton
- Performed initial optical reflectance scanning with static-sample test-bed
- Discrete as well as areal defects and non-uniformities were detected
- Micro-scale variations in image intensity may provide measure of surface porosity





Imaging of discrete (left) and areal (below) non-uniformities

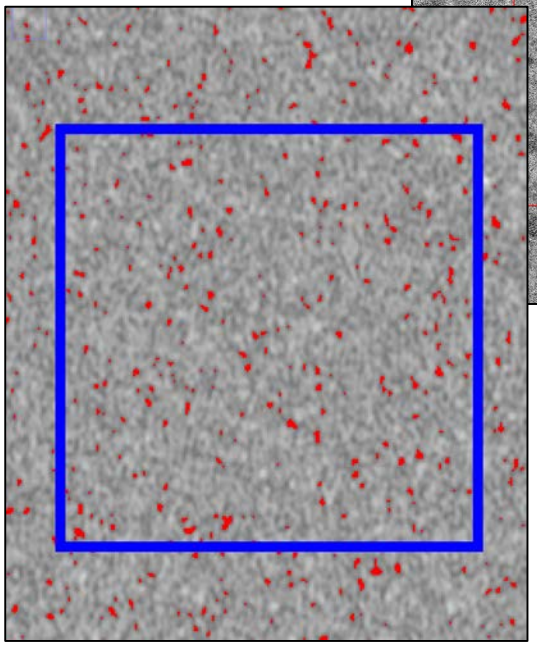


Image showing notional concept of using micro intensity variations (red) to identify surface pores

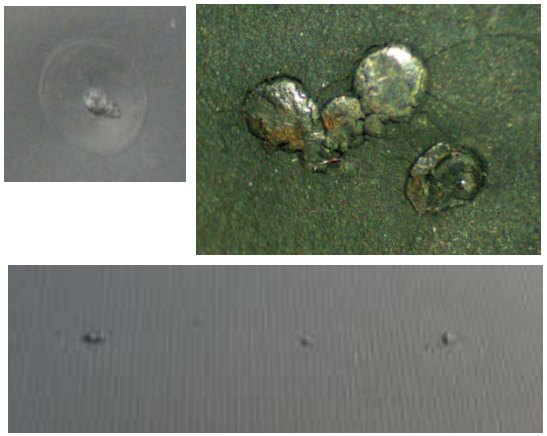
Progress

Further developed defect fabrication methods for in situ studies

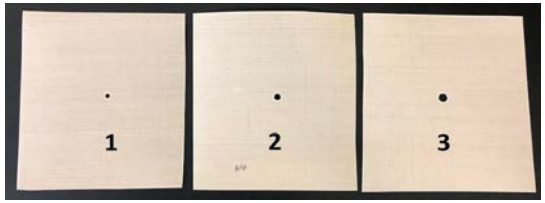
Effects of electrode thick spots

- Follow-on work from last year
- Addressing known process defects
- Two methods to fabricate on CCMs
  - Liquid ink drop-cast
  - Spray coating with mask
- Characterization with optical microscopy shows both methods create features of approximately the same size

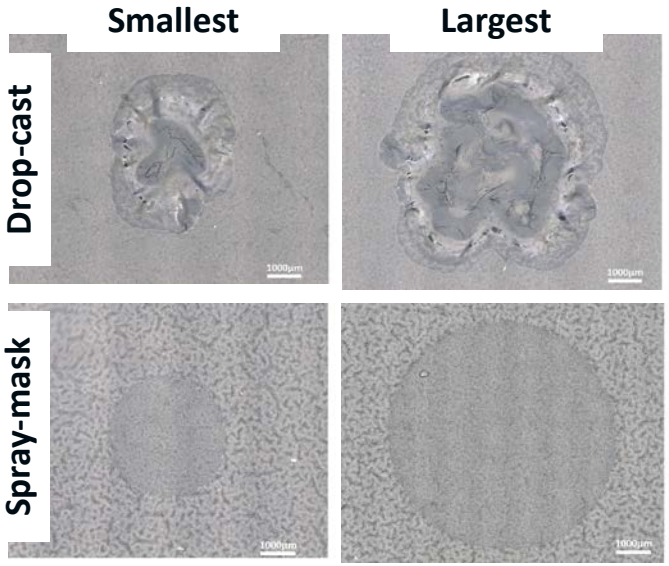
Actual electrode thick spot coating defects



Thick spot fabrication by drop-casting, 3 sizes: 5, 4x 5, 20 µL



Thick spot fabrication by spray mask, 3 diameters: 1.6, 2.4, 3.1 mm



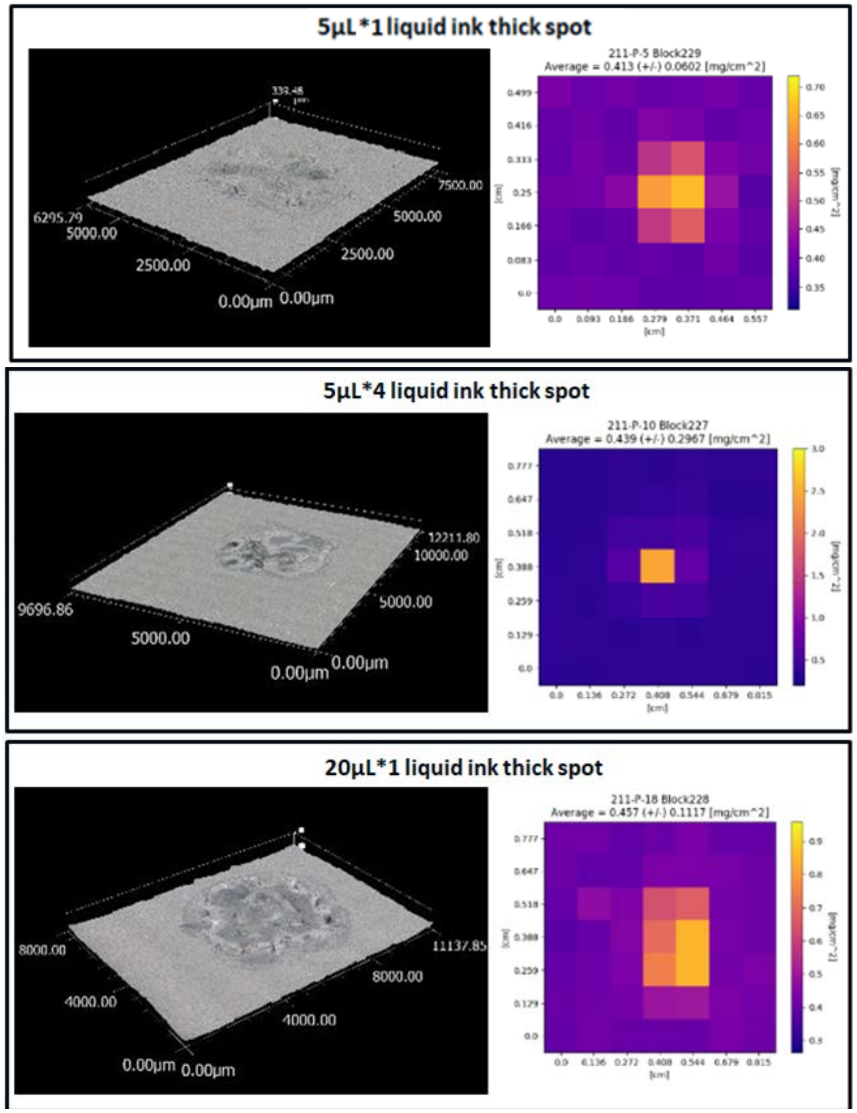
Optical imaging of thick spots fabricated by two methods

Progress

Performed loading and morphology characterization of thick spots

Effects of electrode thick spots

- Performed XRF mapping of Pt to further characterize thick spots
  - Confirm not only the morphology of the thick spot, but increased loading
- In situ testing
  - Drive cycle and AST testing (previously discussed)
  - Impact of thick spot (size, location)
  - Impact of membrane thickness and type
  - Status
    - Testing of pristine baselines with different membranes ongoing
    - Defected cells initiated soon



Microscopy and XRF mapping of drop-cast thick spots

Progress

Preparing for in situ pinhole studies

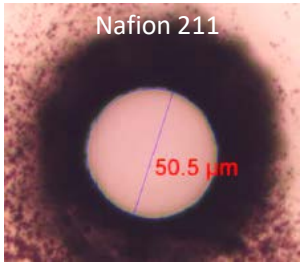
Effects of membrane pinholes

- Follow-on to previous work with Georgia Tech
  - Real casting defects, but can't define sizes
- Use laser drilling to create small holes of definable and repeatable diameter
  - 10, 20, 50 and 100 µm
- Goal is to define threshold of size that impacts performance and lifetime
  - As a function of membrane thickness and type
- We've received samples and are initiating testing
- We'll also study membrane pinhole swelling behavior

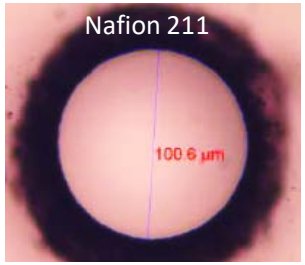
Microscopy validation of pinhole sizes

Pinhole size: 10 µm

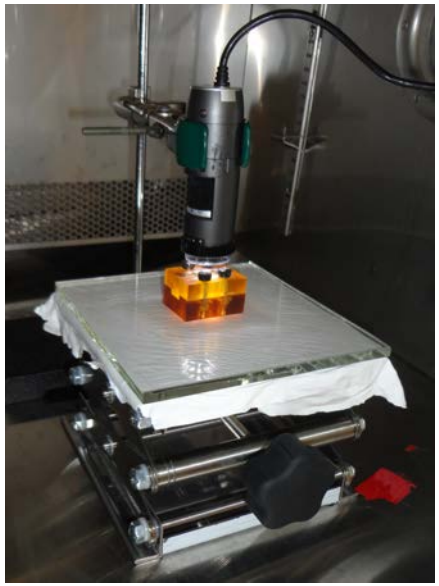
Pinhole size: 20 µm



Pinhole size: 50 µm



Pinhole size: 100 µm



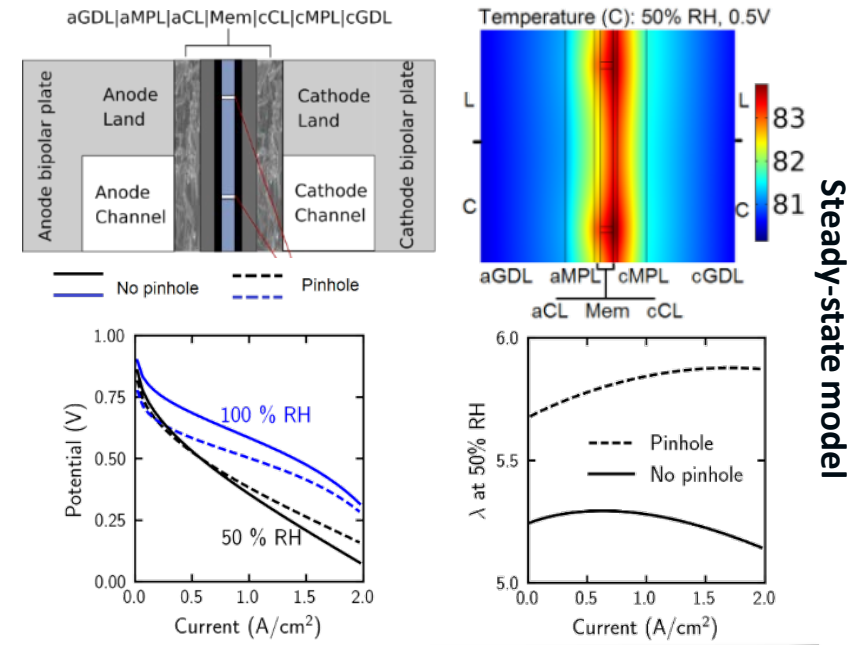
Membrane swelling behavior apparatus

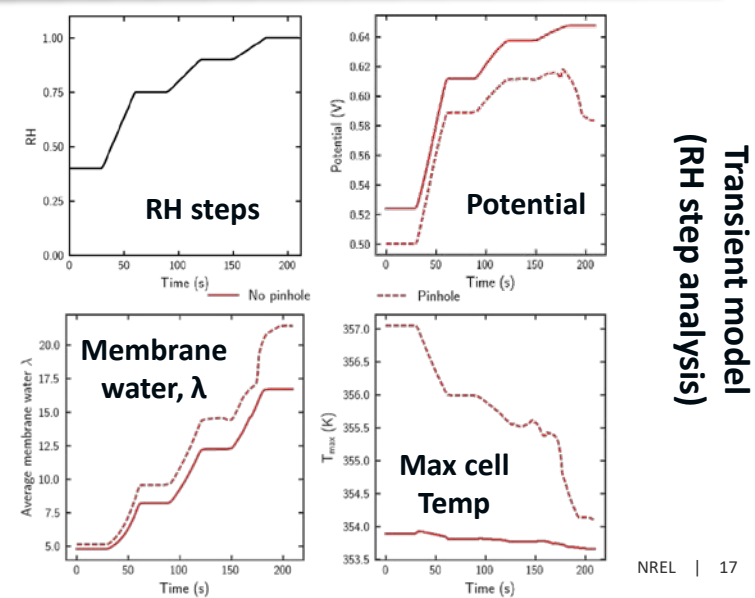
Accomplishments

Predicted impact of membrane pinholes in SS and transient cell operation

LBNL modeling activities to understand and predict impact of membrane pinholes

- Pinhole: 10 µm diameter, membrane: 25.4 µm thick
  - Cell-average results shown (except for spatial temperature plot)
- Steady-state model
  - Complete macro-scale MEA physics with H_2-O_2 reactions
  - Resulting impact of pinholes
    - Local hotspots due to H_2-O_2 reactions in pinholes: durability concern
    - Membrane better hydrated at lower RH due to water production
- Transient model
  - Used current step and RH cycles
  - Resulting impact of pinholes
    - Better hydration observed due to additional water production
    - However, also observe flooding and performance loss in defected MEA
- Mechanical stress modeling: ongoing





Technology Transfer Activities

- SBIR Phase II-b collaboration with Mainstream Engineering (see ta005)
  - Advance QC prototype device to commercializable configuration
- FCTO FOA #1874 project with 3M (see ta026)
  - LTE MEA manufacturing
- H2@Scale CRADA project with HyET (see h2006)
  - EHC MEA manufacturing
- Lab lead for AMO-supported Advanced Materials Manufacturing Roll-to-roll (R2R) Consortium (see ta007)
  - Multi-lab consortium focused on material development, synthesis, process development, and QC/controls development for energy materials by R2R manufacturing
- GM, Gore, Ludlow-PBI, Proton collaborations (discussed above)

Proposed Future Work

"Any proposed future work is subject to change based on funding levels."

Barriers and Needs

- We actively engage with partners to understand their needs, based on their specific processes, materials and MEA constructions
- We attended the aforementioned QC Workshop in Germany, whereat our understanding of barriers and needs was confirmed and expanded
- We will pursue the barriers and needs documented in the MYRD&D Plan

Future Focus

- Continue to work with and gather current information on challenges from as many industry partners as possible in the fuel cell and electrolysis space
  - Initiate new technical activities to address new/unaddressed needs
  - Seek opportunities to implement diagnostics in industry
- Further elucidate the capabilities of multi-spectral imaging for in-line membrane thickness mapping
  - Explore additional uses of this technique
- Apply our QC techniques to new MEA materials and constructions as appropriate, e.g. LTE
- Study the effects of relevant defects on cell performance and lifetime
- Continue to develop and apply predictive models for diagnostics and defects

Summary

- Relevance
  - Domestic and international input
- Approach and Collaborations
  - Continued detailed information exchange with industry partners on QC priorities
- Accomplishments
  - In-line high-resolution scanning and automated defect detection of 1.6 km of Gore membrane
  - In-line demonstration of membrane thickness imaging
    - Scoping study on broad range (thickness, composition) of new membranes
  - Feasibility study (go/no-go) for optical imaging of Pt loading
  - Initial optical scanning of PBI membrane
  - Continued development of thermal scanning for half-cell membrane thickness measurement
  - Demonstration of through-plane IR techniques for LTE CCMs
  - Initial optical scanning study of Ti PTLs
  - Modeling of response of membrane/pinhole to RH
- Progress
  - Preparation for electrode thick spot and membrane pinhole in situ studies
- Tech Transfer
  - Leveraging FCTO investments for many industry-focused projects

Responses to Previous Year Reviewers' Comments

Comments: *"…there does not appear to be a distinct study of how small a defect that can still affect performance might be."*

Response: We thank the reviewer for reaffirming the lack of information regarding this important topic (mentioned ubiquitously at the referenced QC workshop in Germany last fall). We do agree that, despite our efforts over the last number of years, identifying thresholds remains elusive. Our current studies of the performance and lifetime effects of electrode and membrane defects are very focused on this exact need.

Comments: *"…the project team should develop a means to obtain data to ensure future work is aligned with high-frequency defects, performance hits, or other challenges that are limiting the industry's ability to achieve cost and performance targets."*

Response: We absolutely agree that gathering as much current data from industry as possible to confirm or identify manufacturing challenges such as QC needs and understanding of how MEA non-uniformities impact performance and lifetime is a key aspect of our project. It has been all along, and it continues to be a critical focus. As the reviewers may understand, we are not always able to publicly state or show all the information we are given by industry. However, we are gathering this information, with as high a specificity as we possibly can, from many companies on an ongoing basis, including GM, Gore, 3M, Proton, PBI, Advent, and AFC, as well as many other companies in our past interactions. In all cases wherein we use "simulated" defects for our studies, those simulations are intended to represent as directly as possible types of defects that we know to be observed by industry. We also perform studies of actual defected materials from industry partners – we just typically are not able to share those results.

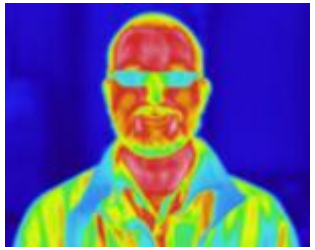
Comments: *"The approach should be to scan commercially produced MEAs or membranes and look for manufacturing defects, study the impact of the discovered defects on fuel cell performance, study ways to quickly screen MEAs and/or membranes for those existing manufacturing defects, and work with the manufacturer to identify the cause of manufacturing defects that have an impact on performance."*

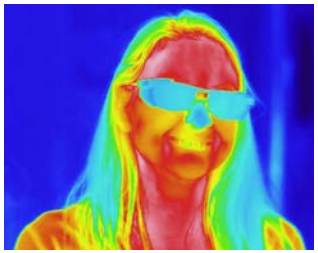
Response: We thank the reviewer for reaffirming our approach. We scan commercially produced MEA materials for manufacturing defects. We study the impact of these discovered defects – sometimes with the actual materials, sometimes with simulations so that we can do designed studies of the impact of size, type, location, etc. We develop rapid in-line measurement methods to image and also automated algorithms to identify defects in real time. We relish opportunities when manufacturers allow us to assist them in identifying root causes, though, understandably, this aspect is often considered highly proprietary and not shared with us.

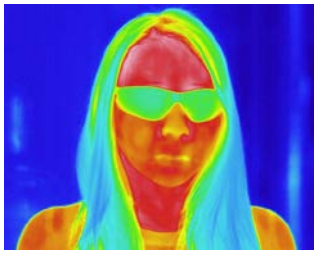
Acknowledgement

NREL

- Guido Bender
- Peter Rupnowski
- Brian Green
- Min Wang
- Calita Quesada







LBNL

- Adam Weber
- Ahmet Kusoglu

CSM

- Prof. Jason Porter
- Derek Jacobsen

Tufts/UCI

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Thank You

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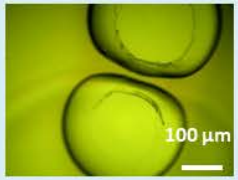
Transforming ENERGY

Technical Back-Up Slides

(Include this “divider” slide if you are including back-up technical slides [maximum of five]. These back-up technical slides will be available for your presentation and will be included in Web PDF files released to the public.)

Overview of diagnostic techniques

Material	Defects	Detection	Resolution (x-y)	Status
Membrane 	Pinholes, bubbles, scratches, agglomerates, etc.	Optical reflectance	micrometers	Demonstrated on web-line
	Thickness variation (mapping)	Optical absorption	micrometers	Demonstrated on motion prototype
		Optical reflectance (interference fringe)	millimeters	In development
		Thermal scanning	millimeters	In development
GDL	Scratch, agglomerate, fibers	IR/direct-current	millimeters	Demonstrated on web-line
Electrode	Surface defects	Optical reflectance	micrometers	Demonstrated on motion prototype
	Voids, agglomerates, cracks, thickness/loading indirectly	IR/direct-current (for CCMs or decals)	millimeters	Demonstrated on web-line
		IR/reactive impinging flow (for GDEs or CCMs)	millimeters	Demonstrated on web-line
	Loading (mapping)	Optical imaging	millimeters	In development
MEA	Shorting	Through-plane IR/direct-current		Demonstrated on motion prototype
	Membrane integrity	Through-plane IR/reactive excitation		Demonstrated on web-line

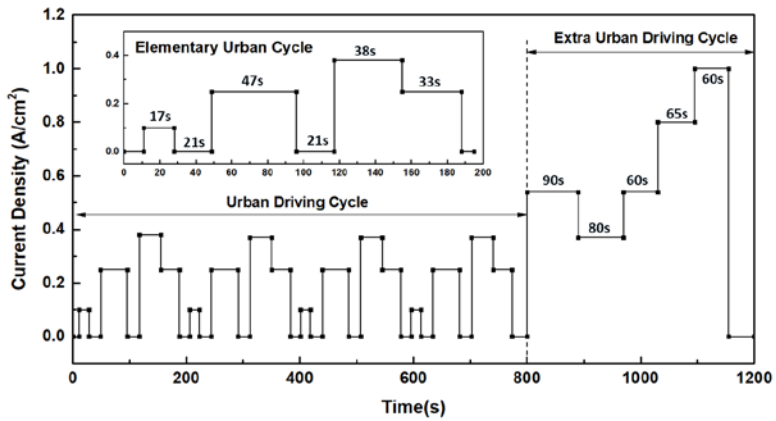
Progress

Further developed drive cycle and AST methodologies for in situ defect testing

Effects of defects: in situ testing details for drive cycle and accelerated stress test

- Drive cycle: improved test station capability and revised script for drive cycle test to match actual referenced cycle (previously implemented cycle had reduced number of peaks per cycle due to test station limitations)

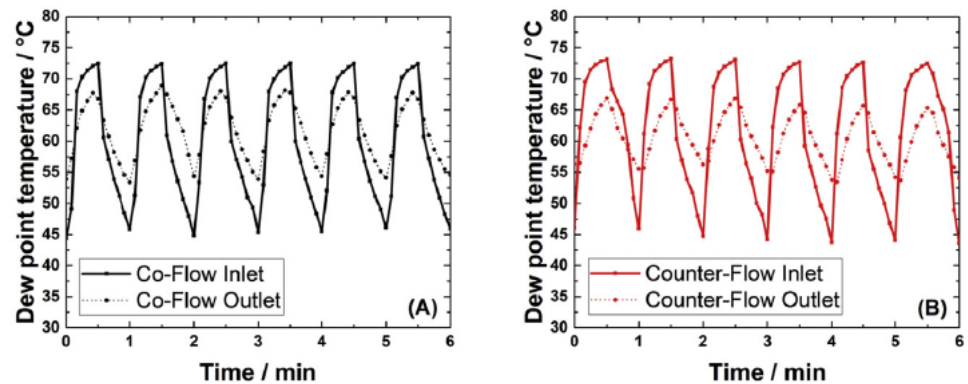
Drive cycle for assessment of performance over time



- NEDC drive cycle testing protocol was built and used
- H_2 crossover LSVs and V-I curve were recorded every 24h

International Journal of Hydrogen Energy, 2010, 35, 2814-2819

AST with spatial hydrogen crossover measurement via IR for assessment of lifetime



The combined AST protocol entailed operating at OCV while cycling the incoming gas humidification between dry and humidified levels. After AST, H_2 crossover limiting current was measured, the IR thermography for spatial H_2 crossover visualization were recorded.

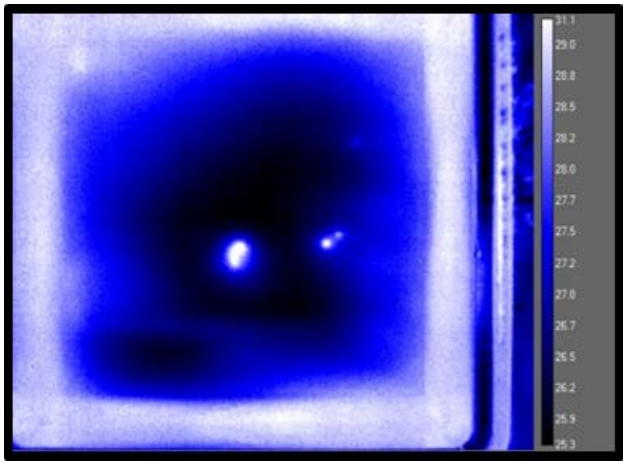
International Journal of Hydrogen Energy, 2018, 43 (12), 6390-6399

Progress

Correlated spatial crossover measurement to actual pinholes via XCT

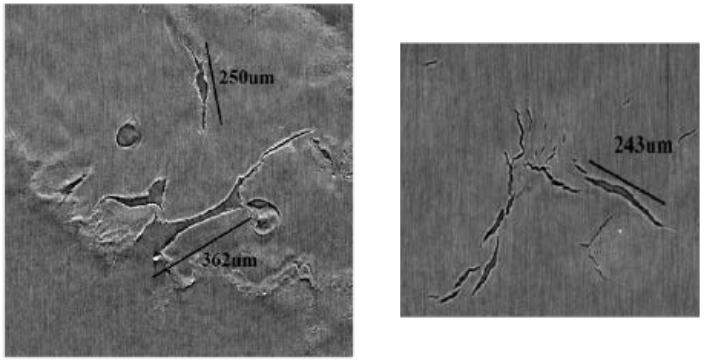
Understanding the impact of failures after aging on MEA morphology with x-ray computed tomography (XCT)

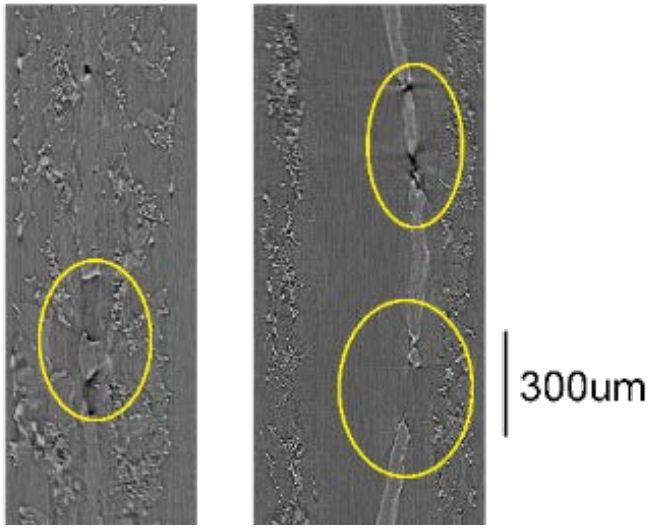
- Imaging at LBNL, ALS, beamline 8.3.2
  - 5x objective lens, 1.3 µm/pixel
- XCT imaging locations identified by post-AST IR imaging of pristine MEA at NREL
- Large pinholes and linear tears are observed, indicating primarily mechanical degradation
- These methodologies will be used on MEAs with beginning-of-life defects



Post-AST spatial hydrogen crossover measurement via IR thermography

In-plane images of membrane tears



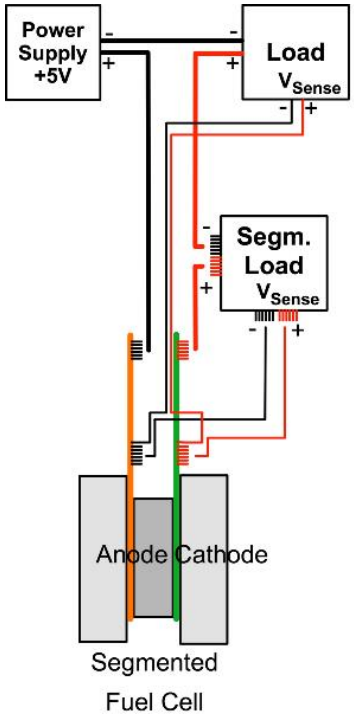
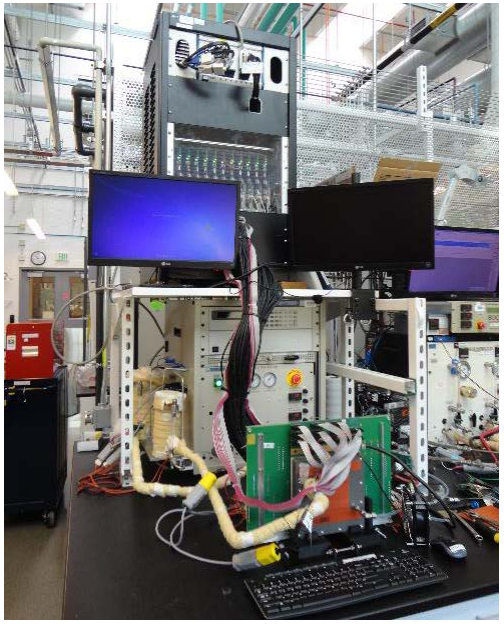
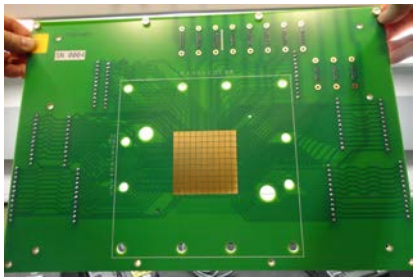


MEA cross-sections showing pinholes and tears

Update on Segmented Cell GEN 2

Key elements of NREL segmented cell system

- 121 segments in 50 cm^2 area (0.413 cm^2 segment size)
- Current density up to 2.4 A/cm^2
- Custom software with visual and numerical data presentation & analysis features

Benefits of GEN 2 Updates

- Cell now operates as a true single cell, with a natural current and voltage distribution
  - Spatial sensing only, not voltage or current control
  - i.e. can break in and run cells on single-cell test stations, then move entire cell hardware to segmented cell for spatial characterization
- Interchangeable flow-fields (not possible in previous design)
  - Large manifold area
  - Current: Quadruple serpentine, triple parallel
- 4-wire measurements on all segments
- Improved cell sealing